

# PATENT SPECIFICATION

(1) 213 122

NO DRAWINGS

- (21) Application No. 40683/66 (22) Filed 12 Sept. 1966  
 (21) Application No. 40684/66 (22) Filed 12 Sept. 1966  
 (21) Application No. 40685/66 (22) Filed 12 Sept. 1966  
 (23) Complete Specification filed 11 Dec. 1967  
 (45) Complete Specification published 18 Nov. 1970  
 (51) International Classification C 01 b 33/22  
 (52) Index at acceptance

C1A D41 G12 G12D41 G44 G48 G50  
 C3N 25 2A1 X  
 C5F 431 C

(72) Inventor BARBARA SUSAN NEUMANN



## (54) CLAYS

(71) We, LAPORTE INDUSTRIES LIMITED, a British Company, of 14 Hanover Square, London W.1, formerly known as The Fullers' Earth Union Ltd. a British Company of Pateson Court, Nutfield Road, Redhill, Surrey, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

Most clay minerals, as found naturally, are in an impure state and the complete purification of some is difficult and expensive and, in some cases, impossible. Further, there are occasions on which the supply of a clay mineral of a particular chemical composition, either pure or impure, is insufficient. Thus, it is desirable to be able to manufacture synthetic clay-like minerals in a substantially pure form.

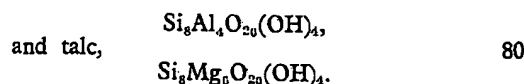
It is of particular interest to be able to manufacture synthetic clay-like minerals having rheological properties similar to or better than those of hectorite, as natural hectorite has valuable properties but large quantities of hectorite are not available. In any event natural hectorite is mixed with impurities the removal of some at least of which is extremely difficult.

We have described in our Specification No. 1054111 one method of synthesising hectorite-type clay minerals and to our knowledge only two other methods are known which are capable of yielding more than a few milligrams of product under conditions which are feasible on a commercial scale. One method is described by Granquist and Pollak in Clays and Clay Minerals, Natl. Acad. Sci., Natl. Res. Council Publ. 8. 150—169, (1960) and the other is described by Strese and Hofmann in Z. Anorg. Chem. 247, 65—95, 1941. It is not possible, by either of these methods, to obtain products that are entirely

pure. Thus, the product of Strese and Hofmann's method contains a high proportion of amorphous silica or silicate and some crystalline silica, or quartz. The removal of the amorphous substance is impossible and any product obtained by this method necessarily contains such a high amount of impurity that the rheological properties of aqueous dispersions of the product are adversely affected. The product obtained by the method described by Granquist and Pollack contains some magnesium hydroxide. The removal of this is difficult and it is probably impossible to remove it all. It is known that the presence of even quite small amounts of magnesium hydroxide harms the rheological properties of aqueous dispersions of clay minerals.

Many clay-like minerals contain fluoride but however much they are purified there is always a risk that some fluoride may be extracted from the mineral during certain uses. This is a great disadvantage in, for example, pharmaceutical and cosmetic preparations. The present invention is of particular value in that it readily permits the production of fluoride-free clay-like minerals, and, moreover, such swelling clays which are fluoride-free.

One class of natural clay minerals are the smectites, including montmorillonite, beidellite, nontronite, sauconite, saponite and hectorite. The elementary structure of these minerals may be based on that of the two end members of the series which are themselves not clay minerals,rophyllite,



In clay mineral structures some at least of the silicon, aluminium or magnesium and hydroxyl ions are replaced by other ions. As

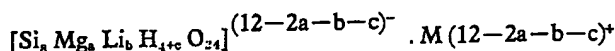
1213 122

a result of the first two types of substitution the structure shown may acquire a negative charge, which is neutralised by associated exchangeable cations, frequently alkali metal cations. Thus, the silicon may be replaced by aluminium, the aluminium by ferrous iron or magnesium, the magnesium by lithium and the hydroxyl by fluoride. In natural hectorite part of the magnesium is generally replaced by lithium and a minor part of the hydroxyl is replaced by fluoride. Sometimes part of the silicon is replaced by aluminium.

According to the invention we can now provide new synthetic silicates having a structure similar to that of clay minerals of the smectite type. Thus the new synthetic silicates have X-ray diffraction patterns similar to those of the clay minerals discussed above and, being synthetic, can be considered to be clay-like minerals. Although the new synthetic silicates have X-ray diffraction patterns similar to those of the corresponding natural clay aqueous dispersions of the new silicates

have rheological properties that are very much better than natural clays. In particular they have Bingham Yield Values, as 2% dispersions in tap water, very much higher than the Bingham Yield values of natural clays of the smectite type and very much higher than the Bingham Yield Values of silicates made by the method of Granquist and Pollak, or by the method of Strese and Hofmann described above. Also the new silicates may have swelling properties greater than those obtained in the processes of Specification No. 1,054,111. This is indeed surprising since it is critical in that process to employ fluoride-containing materials above a certain minimum level whereas the new silicates are free of fluoride. Because of their freedom from fluoride the silicates are of particular value in the cosmetic and pharmaceutical fields.

The synthetic silicates according to the invention have a structure similar to that of clay minerals of the smectite type and have the general formula



having

- (i) M as a sodium, a lithium or an equivalent of an organic cation, and
- (ii) the value of a, b and c such that either

$$a < 6; b > 0; c > 0;$$

and

$$b + c < 2; \pm(a + b + c - 6) < 2;$$

or

$$a < 6; b = 0; \pm c < 2;$$

and

$$\pm(a + c - 6) < 2$$

The new synthetic silicates are further characterised in that they have a cation exchange capacity of 50 to 120 m.e.q./100 g and in that, when M is Na or Li<sup>+</sup>, they have a Bingham Yield Value of 40 to 250 dynes/cm<sup>2</sup> as a 2% dispersion in tap water.

The term Bingham Yield Value is also known as Bingham Yield Stress (these terms being alternatives for precisely the same property) and is referred to in such standard works on Rheology as "Rheology Theory and Applications", ed. F. R. Eirich (Acad. Press) Vol. 1 (1956) p. 658; "Colloidal Dispersions", L. K. Fischer (N. Y. Bureau of Standards), 2nd Edn. 1953, pps. 150—170, and "The Chemistry and Physics of Clays and Other Ceramic Materials", 3rd Edn., p. 463, A. B. Searle and R. W. Grimshaw. The term may be defined as the shear stress which has to be exceeded before the rate of shear shows a linear relationship to the shear stress, the former being proportional to the difference between the shear stress and the Bingham Yield Value.

The Bingham Yield Value is determined by first obtaining a flow curve relating the shear stress to the rate of shear, and then extrapolating the straight line section of the curve to the shear stress axis; the intercept is the Bingham Yield Value. It can be conveniently determined on any Viscometer capable of measuring a range of shear rates and shear stresses. In the experimental work quoted in the present specification a Fan rotational Viscometer was used in the manner set out in the book "Oil Well Drilling Technology" by A. W. MaCray and F. W. Cole Union of Oklahoma Press, p. 94—96 (1958). When measured on this instrument the results are in the unit of lbs/100 sq.ft. However in this specification the more usual unit of dynes/cm<sup>2</sup> will be used. As is well known, to convert lbs/100 sq.ft. to dynes/cm<sup>2</sup> a multiplication factor of 4.8 must be used.

A separate feature of the invention resides in a process for the production of synthetic silicates having the general formula and the values of M, a, b and c defined above. This process comprises

(i) precipitating a magnesium silicate having the value of "a" desired in the said synthetic silicate by combining an aqueous solution of a water soluble magnesium salt with an aqueous alkaline solution of one or more sodium compounds in the presence of dissolved silicon-delivering material, the pH of the alkaline solution being maintained at 8 to 12.5 throughout,

(ii) without first drying or washing this precipitate heating it at a temperature of at least 170°C and a pressure of at least 100 p.s.i., the temperature being less than 370°C

and such that a liquid phase is present, until crystal growth occurs, and

(iii) separating the resultant solid and liquid phases.

5 The relationships between a, b and c quoted above are a "shorthand" way of signifying that in all cases the number of magnesium ions per unit cell of crystal is less than  
10 six and the total number of octahedral ions does not differ from six by more than two. If there is lithium present, the total number of hydrogen ions, including those normally assumed to be present as hydroxyl, is greater than or equal to four and the total number  
15 of octahedral ions other than magnesium is less than two. If lithium is absent, the total number of hydrogen ions may not differ from four by more than two.

20 The Bingham Yield Values quoted above relate to values in tap-water. However it is the case that the Bingham Yield Value of the synthetic clay dispersions depend to a large extent on the concentration and type of electrolyte present in water. The general  
25 effect is such that addition of electrolyte to a dispersion of synthetic clay made in distilled water or tap water at first increases then decreases the BYV. The maximum value, obtained at optimum electrolyte concentration is several times higher than that prevailing  
30 the dispersions made in the local tap water. This effect will be illustrated hereinafter.

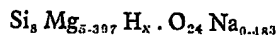
In addition to being free from fluorides, the new materials according to the invention  
35 are substantially pure, being substantially free of magnesium hydroxide, amorphous silica or silicate and other impurities. By substantially pure we mean that the clays are either wholly free of the impurities or only contain such  
40 small amounts that the Bingham Yield Value of aqueous dispersions of the materials is within the range specified. The Bingham Yield Value is preferably at least 50 and most preferably at least 75 dyne/cm<sup>2</sup> (as a  
45 2% dispersion in tap water). The materials may contain, at the most, 5 to 10% by weight impurities but the impurities will always be such and the amounts of them will be such that x-ray analysis does not  
50 reveal their presence. Thus, any impurities that are present in more than trace quantities will be amorphous. The major part of any impurities generally consists of non-crystalline material, having the same formula  
55 as the crystalline material.

In this specification we always mean that the Bingham Yield Value is the value obtained with a dispersion made by dispersing 2 gm. of the material in 100 ml. hot tap water and allowing the dispersion to cool. The tap water we use has a hardness of about 140 p.p.m.

60 The Bingham Yield Values generally of at least 75 dyne/cm<sup>2</sup>, compare with values  
65 of less than around 15 dyne/cm<sup>2</sup> for products

made by the process of Granquist and Pollack even when magnesium hydroxide originally present in the product has apparently all been removed, based on the evidence of x-ray analysis, and for the products prepared  
70 by the method of Strese and Hofmann and for naturally occurring hectorite. The crystal structure of the new materials as determined by x-ray analysis is similar to that of natural hectorite and it is not possible to identify,  
75 by readily available experimental methods, exactly what the characteristics are of the microstructure and chemical composition of our new materials that results in them having such high Bingham Yield Values when dispersed in water. However, by choosing appropriately the proportions of the components in the solution from which the clays are co-precipitated, and thus the ratios of the atoms in the materials, and the conditions of the process synthetic materials having Bingham Yield Values even greater than 75 dyne/cm<sup>2</sup> may readily be obtained. Thus, synthetic materials having Bingham Yield Values of more than 100, and often more than 150  
90 and sometimes even more than 250 dyne/cm<sup>2</sup> may be obtained, especially in the materials containing lithium. These values are as 2% dispersions in tap-water. The values can be increased as discussed above.  
95 The preferred new clay-like minerals have a very high specific surface area. Generally, it is at least 100 sq. m./gm. and often 350 sq. m./gm., or more, although clearly it should not be too high. This compares to a value of around 70 sq. m./gm. for natural hectorite.

From a study of the formula given above for the preferred new synthetic materials it will be appreciated that it is contemplated that there may be more or fewer hydrogen atoms than the four required for the four hydroxyl groups that would be expected to be present in a fluoride-free hectorite molecule according to the traditional concept of smectite structure. The evidence for this possibility is based on the fact that many of the preferred materials have a cation exchange capacity which could not be reconciled with the conventional formula, although the latter is applicable to natural hectorite or the synthetic hectorites made by the two known processes discussed above. The cation exchange capacity of the preferred materials according to the invention may be, for example, 64 milliequivalents per 100 gram and the chemical analysis equivalent to  
120



where x is not readily determined by analysis. The cation exchange capacity can only be made to agree with the composition if one assumes that  $x=4.723$ , i.e.  $c=0.723$  according to our formula quoted above. The conventional formula would require a cation ex-  
125

change capacity of  $2(6-5.397)=1.206$  equivalents per unit cell, or about 160 milliequivalents per 100 gram which is very much greater than the experimentally measured value. In general, the new materials may have cation exchange capacities falling within the range 50 to 120 meq/100 gm., normally 60 to 90, and this is highly desirable.

A high proportion of magnesium, lithium and silicon ions present in the solution from which the materials are coprecipitated go into the materials formed and accordingly adjustment of the relative ratios of the quantities of these ions will result in variations of the empirical formula of the material formed. The proportion retained is even higher than in the process of our earlier invention and thus represents an even more economical use of material.

For the production of the preferred, fluoride-free, materials having satisfactory Bingham Yield Values and containing lithium it is preferred that the quantities in the solution should be such that there are from 0.4 or 0.6 to 1.45 lithium atoms per 8 silicon atoms and preferably from 0.6 to 1.2 Bingham Yield Values of greater than 100 may be obtained in this way. Bingham Yield Values greater than 150 may be obtained with solutions containing from 0.7 to 1.45 lithium atoms per 8 silicon atoms. In the final product it is preferred that the number of lithium atoms per unit cell (i.e. 8 silicon atoms) is between 0.6 and 1.05.

When the solution and the material to be coprecipitated from it are free of lithium it is preferred that there should be fewer than 6 magnesium atoms per 8 silicon atoms in the solution and product. For satisfactory Bingham Yield Values the deficiency of magnesium is preferably at least 0.1 atoms per unit cell, but is generally not more than 1.5 atoms per unit cell. Preferably the deficiency is more than 0.2 and most satisfactory results are obtained with magnesium deficiencies of from 0.5 to 1 atoms per unit cell with the preferred deficiency being around 0.7. Thus when  $b=0$ , a preferably equals about 5.3.

Any suitable magnesium and lithium salts may be used for introducing these cations into the solution. Examples are magnesium chloride, magnesium sulphate, magnesium nitrate, and lithium chloride, sulphate and nitrate. The reaction solution must remain alkaline throughout the coprecipitation and so must contain sufficient alkali to neutralise anions liberated during the coprecipitation, for example to neutralise sulphate ions liberated from magnesium sulphate. Thus preferably more than the stoichiometric amount of alkali required to neutralise both the anions liberated during the reaction and also the anion of the clay molecule is present in the reaction solution. The amount

is preferably between the stoichiometric amount and 3 times the stoichiometric amount, with the preferred amount being about  $1\frac{1}{2}$  times.

The coprecipitation is preferably brought about by mixing a hot solution containing the magnesium salt, and any lithium salt that is to be included, with a cold solution containing the silicon. This cold solution generally also contains the alkali. The silicon may be introduced in the form of any suitable silicate. The addition of one solution to the other may be made rapidly or slowly, but we find it satisfactory to make the addition over a period of around 20 minutes.

The properties of the material obtained do not seem to vary much with the concentration of the reactants used, and accordingly the concentration of the precipitate formed. However, for experimental reasons it is generally preferred to select the concentrations of the reactants so that the concentration of precipitate is not more than 5% by wt. Above this value difficulties are experienced in filtering and washing the precipitate.

The precipitate may be boiled after it is formed, and before it is heated under pressure, to facilitate subsequent handling of the precipitate. Particularly it facilitates washing and filtering of the precipitate. Boiling periods of around 4 hours are found to be satisfactory.

The heating under pressure is conducted in an autoclave and is normally conducted at the autogenous temperature. The pressure is at least 100 p.s.i. (170°C) if lithium is present with suitable pressures of from 150 to 700 p.s.i. (186°C to 263°C). The temperatures quoted are the autogenous temperatures. Pressures from 700 to 1000 p.s.i. are advantageous when, as referred to hereafter, an organic derivative is subsequently to be prepared. However, when this is not the case then good results may be obtained with pressures of from 200 to 600 p.s.i. (198°C to 254°C). One suitable pressure that we have found is around 400 p.s.i. (231°C). When lithium is absent the lower pressures mentioned are not entirely satisfactory and in general the pressure has to be at least 250 p.s.i. (207°C). A suitable range of pressures, when there is no lithium, is 500 to 1000 p.s.i., with a value of around 700 being preferred. However in all cases there is no critical upper limit, except that a liquid phase should exist throughout and thus the temperature should be kept below the critical temperature, i.e. below 370°C. The higher pressures and temperatures up to this point may be desirable as a means of reducing the time required for the process. This may then enable a continuous process to be operated, feeding in and bleeding off through suitably constructed and arranged valve means.

The autoclaving results in crystallisation of

the clay-like mineral and if it is continued for too long too much crystallisation occurs and the rheological properties of aqueous dispersions of the product are adversely affected. The autoclaving, especially when at 400 p.s.i., should be continued, however, for at least one hour, but generally eight hours is quite long enough. A preferred duration is around four hours. However, when as referred to in more detail later, an organic derivative is subsequently to be prepared then it may sometimes be preferred to continue the autoclaving for as much as 24 hours.

The product from the autoclaving is generally a suspension. The solids are usually separated by filtration or centrifuging and washed, for example with water, to remove soluble by-products, such as sodium sulphate, from the coprecipitation. This wet product may then either be used, for example in chemical reaction, as such or it may be dried. The drying may be dry, for example, heating at 110°C for sixteen hours.

In the following examples, Examples 1 and 2 demonstrates the production of new materials according to the invention and which have an x-ray diffraction pattern similar to that of hectorite and which are free of fluoride but contain lithium. Example 2 also illustrates the variation in Bingham Yield Value with increase in electrolyte. Example 3 is a comparative Example and demonstrates that on increasing the lithium content up to 1.75 atoms per unit crystal Bingham Yield Value is decreased and Example 4 is another comparative Example and shows that lithium contents greater than 2 give no appreciable Bingham Yield Value. Examples 5 and 6 are examples of the production of a material free both of lithium and fluorine. Example 7 illustrates a very high pressure/short time process.

Example 8 is a comparative Example of a process based on the Strese and Hofmann paper referred to above, particularly as described in pages 73 and 78 to 80 thereof. Example 9 is a similar process to Example 8, but using the quantities described Example 2. These Examples show that the method of Strese and Hofmann gives very poor results.

In all examples the cation exchange capacity of the products was measured by the method according to R. C. Mackenzie, in J. Colloid Sci., 6, 216 (1951).

## EXAMPLES

### EXAMPLE 1

130.7 g. magnesium sulphate heptahydrate and 2.97 g lithium chloride were dissolved in 900 ml. water in a flask of about 5 litres capacity and heating to boiling point. In a separate vessel 38.6 g. sodium carbonate was dissolved in 900 ml. water and 166 g. sodium

silicate solution containing 25 g.  $\text{SiO}_2$ , and 8.8 g.  $\text{Na}_2\text{O}$  per 100 g. was added to it. The second solution was added to the first, when it was observed that a white precipitate was formed. The mixture was brought to the boil under reflux while stirring efficiently. After boiling for two hours, the contents of the flask were transferred to an autoclave fitted with a stirrer, heated in  $\frac{1}{2}$ —1 hour to 250°C. corresponding to a gauge pressure of 562 pounds per square inch, and held at that temperature for 4 hours, while being continuously stirred. The mixture was then allowed to cool below 100°C, discharged from the autoclave and the solids present were filtered and washed with tap water by filtration until the filtrate showed no significant sulphate reaction when tested with barium chloride solution. The filtercake was dried in an oven at 110°C for 16 hours and ground to a powder.

The product had  $M=\text{Na}^+$ ,  $a=5.29$ ,  $b=0.47$ ,  $c=0.49$ .

When 2 g of the powder was dispersed in 100 ml. hot tap-water (containing 39 p.p.m.  $\text{Ca}^{++}$  and 4 p.p.m.  $\text{Mg}^{++}$ ) it was found that, after cooling, a white translucent gel was obtained. By using a rotational viscometer (Fann VG model), the following rheological parameters were measured on this dispersion:

Plastic viscosity	13 centipoises	
Bingham Yield Value	72 dyne/cm <sup>2</sup>	95

The cation exchange capacity was found to be 0.59 milliequivalents per gram. X-ray analysis by the powder diffraction method showed that the structure corresponded to that of natural hectorite and no other crystalline material could be detected. Differential thermal analysis gave a pattern similar to that of natural hectorite having only endothermic peaks in the 600—800°C. range.

### EXAMPLE 2

The same procedure was followed as in Example 1, but altering the quantity of certain of the constituents. Thus there was employed 122.0 g. magnesium sulphate heptahydrate and 4.45 g. lithium chloride.

The product had  $M=\text{Na}^+$ ,  $a=5.03$ ,  $b=0.63$ ,  $c=0.78$ .

The cation exchange capacity was 0.67 meq/g. X-ray analysis showed the same pattern as hectorite and differential thermal analysis in the 600—800°C. range showed only endothermic peaks.

A dispersion of 2 g. of the product in 100 ml. of hot tap-water gave after cooling an almost clear thixotropic gel giving a plastic

viscosity of 18 centipoise and a Bingham Yield Value of 210 dyne/cm<sup>2</sup>.

The BYV of this dispersion was measured again after adding various amounts of sodium sulphate in the form of a concentrated solution. The following results were obtained:

	Amount of Na <sub>2</sub> SO <sub>4</sub> added as milliequivalents per litre dispersion containing 2% synthetic clay	BYV (dyne/cm <sup>2</sup> )
10	10	400
	20	520
	30	550
	40	565
15	60	520
	100	400
	150	180

#### EXAMPLE 3

Again the same procedure was followed as in Example 1, but the amount of magnesium sulphate heptahydrate employed was 105.0 g. and the lithium chloride 7.42 g.

The product had  $M=Na^+$ ,  $a=4.63$ ,  $b=0.82$ ,  $c=1.42$ , i.e.  $b+c=2.24$ .

A dispersion of 2 g. product in 100 ml. hot water gave after cooling a white opaque thixotropic gel having a plastic viscosity of 13 centipoise and a Bingham Yield Value of 38 dyne/cm<sup>2</sup>. The cation exchange capacity was 0.65 meq/g. X-ray analysis gave the hectorite pattern, but the diffraction lines

were more diffuse than those given by the products of Examples 1 and 2. Differential thermal analysis showed both endothermic peaks in the 600—800°C range, the exothermic peak being sharp and relatively small compared with the endothermic peak.

#### EXAMPLE 4

Again the same procedure was followed as in Example 1, but the amount of magnesium sulphate heptahydrate was 96.1 g. and the lithium chloride 8.90 g.

The product had  $M=Na^+$ ,  $a=4.42$ ,  $b=0.92$ ,  $c=1.71$  i.e.  $b+c=2.63$ .

When 2 g. of the product was dispersed in hot water, it was found that the solids settled almost immediately after stirring had ceased and no thixotropic gel could be obtained.

The cation exchange capacity was 0.69 meq/g. X-ray analysis gave a very diffuse hectorite like pattern with a high degree of scatter indicating poorly crystallised or amorphous material. Differential thermal analysis showed both exothermic and endothermic peaks between 600—800°, the two types being of similar magnitude.

The amounts of chemicals used in Example 1—4 were calculated to supply silicon, magnesium and lithium in the following atomic ratios:—

Example	Si	Mg	Li	Bingham Yield Value
1	8	5.3	0.70	72
2	8	4.95	1.05	210
3	8	4.25	1.75	38
4	8	3.90	2.10	0

At the same time, the amount of sodium carbonate was calculated by the formula given below:—

$$W = 0.882 p \frac{(1.5r - 1)}{r}$$

where W is the amount in grams of Na<sub>2</sub>CO<sub>3</sub> required per 100 g. sodium silicate used, if the concentration of SiO<sub>2</sub> in the sodium silicate is p% (w/w) and the molar ratio of SiO<sub>2</sub> to NaOH is r.

#### EXAMPLE 5

The same procedure was followed as in Example 1, but the amount of magnesium sulphate heptahydrate was 139.3 g., no lithium chloride was employed and the amount of sodium carbonate was 42.5 g.

The product had  $M=Na^+$ ,  $a=5.09$ ,  $b=0$ ,  $c=1.38$ .

A dispersion of 2 g. product in 100 ml. hot water gave after cooling an almost clear colourless thixotropic gel having a plastic viscosity of 12 centipoise and a Bingham Yield of 95 dyne/cm<sup>2</sup>. The cation exchange capacity was 0.55 meq/g. X-ray analysis gave the typical hectorite pattern. Differential thermal analysis showed large exothermic and endothermic peaks in the 600—800°C range.

The chemicals used in this Example were calculated to supply silicon and magnesium in the atomic ratio of 8:5.65. The sodium carbonate added was that calculated by the formula given after Example 4, plus 10% excess.

#### EXAMPLE 6

125.7 g. magnesium sulphate heptahydrate was dissolved in 630 ml. water and heated to boiling point. In a separate vessel 38.7 g. sodium carbonate was dissolved in 630 ml. water and 166 g. sodium silicate of the type

used in the other Examples was added to it. The second solution was added to the first under continuous stirring over a period of 30 minutes. The mixture was boiled under reflux for two hours, then heated to 286°C (corresponding to a gauge pressure of 1000 p.s.i.) and held at that temperature for 4 hours while being stirred. The subsequent treatment was the same as that used in all the previous Examples.

The product had  $M=Na^+$ ,  $a=5.38$ ,  $b=0$ ,  $c=0.78$ .

The rheological parameters of the product were:—

15	Bingham Yield Value	152 dyne/cm <sup>2</sup>
	Plastic Viscosity	13 centipoise
	Cation exchange capacity	0.63 meq./g.

After adding some concentrated Na<sub>2</sub>SO<sub>4</sub> solution to raise the electrolyte content of the solution to 45 meq./litre, the BYV rose to a maximum of 382 dyne/cm<sup>2</sup>.

#### EXAMPLE 7

In this example, initially the same procedure was followed as in Example 2, but the amount of water used for making up the two solutions was 630 ml. instead of 900 ml. The slurry containing the precipitate was heated as rapidly as possible to 336°C corresponding to 2000 p.s.i. (total heating time from boiling point 2½ hours), and immediately cooled as rapidly as possible by standing the autoclave in cold water. The product was then treated as all other preparations and it was found that it had the following properties:—

BYV	40 dyne/cm <sup>2</sup>
p.v.	5 centipoise

The maximum BYV at optimum electrolyte concentration was 475 dyne/cm<sup>2</sup>. The cation exchange capacity was 0.70 meq./g.

#### EXAMPLE 8

122 g. magnesium sulphate heptahydrate was dissolved in 450 ml. water and in another vessel 166 g. sodium silicate solution of the kind used in Examples 1—5 was mixed with 450 ml. water. The second solution was added to the first and the resulting precipitate was washed by filtration till it was sulphate free. It was then dried at 110°C for 16 hours, ground and subsequently mixed with 600 ml. of 2N solution of sodium hydroxide. The resulting mixture was transferred to an autoclave and heated for 36 hours at 240°. After cooling, the solids were washed by filtration until the filtrate was almost free from alkali; finally the product was dried at 110°C and ground.

When 2 g. of the product was dispersed in hot water, it was found that part of the material settled almost immediately, while the remainder formed after cooling a white opaque weak gel having a plastic viscosity of 6 centipoise and a Bingham Yield Value of 14 dyne/cm<sup>2</sup>. The cation exchange capacity was 0.55 meq./g. X-ray analysis gives a complex pattern containing faint and diffuse lines of hectorite and much stronger and sharper lines of at least one other crystalline substance, mainly quartz. Differential thermal analysis showed only small exothermic and endothermic peaks between 600°—800° C.

The amount of chemicals used in this preparation correspond to a Si/Mg. atomic ratio of 1.6. The amount of sodium hydroxide is considerably higher than the equivalent amount of sodium carbonate calculated according to the formula given after Example 4.

#### EXAMPLE 9

In this experiment, the same amounts and types of chemicals were used as in Example 2, while the method followed was the same as in Example 8. Thus the magnesium sulphate and sodium silicate solutions were mixed to form a precipitate which was then washed, dried and redispersed in 600 ml. solution containing the sodium carbonate and lithium chloride. After autoclaving, washing, drying and grinding, as in Example 8, the product was tested and gave very similar results to Example 8.

Plastic viscosity at 2% conc.	10 centipoise
Bingham Yield Value at 2% conc.	14 dyne/cm <sup>2</sup>
Cation exchange capacity	0.69 meq./g.
X-ray analysis	weak hectorite strong quartz pattern. as example 8.
DTA	

All the synthetic clay-like minerals discussed in detail above have an inorganic cation M, but useful derivatives in which the cation is organic may be made. Thus the inorganic materials may be converted into new synthetic clay mineral organophilic products in which at least some of the exchangeable cations consist of one or more organic cations endowing it with an organophilic nature. These new organophilic products may be prepared by reacting one of the new synthetic clay minerals, either before washing, after washing or after drying, in a liquid, preferably aqueous, medium with an organic compound or salt thereof which gives rise in the medium to an organic cation capable of undergoing a cation exchange reaction with the synthetic clay. Preferably at least a major part of the exchangeable cations

in the organophilic product are of the specified organic cations.

5 Examples of organic compounds or salts thereof from which such cations may be derived are to be found among the following classes:— organic ammonium, organic phosphonium, organic stibonium, organic arsonium, organic oxonium, organic sulphonium.

10 In general, the cations of prime importance as far as the present invention is concerned are based on nitrogen, i.e. the organic ammonium salts. By way of example this class of compounds includes the salts (including quaternary salts) of primary, secondary  
15 and tertiary amines, including mono-, di-, tri and polyamines as well as aliphatic, aromatic, cyclic and heterocyclic amines and substituted derivatives thereof. Other mono- or polyvalent compounds which are of particular value in the practice of the present invention are the so-called "Ethomeens" (Armour  
20 Company "Ethomeen" is a trade mark). These compounds may be regarded as tertiary amines having a single alkyl group and two polyoxyethylene groups attached to the nitrogen atom. Similarly the products sold under the trade mark "Ethoduomeen" (Armour & Company) are also of value.

30 Preferably, the organic radical present has at least ten carbon atoms, desirably at least twelve and advantageously at least eighteen. The compounds may have up to 30, 40 or even 50 or more carbon atoms depending on the availability of such materials.

35 Specific examples of suitable organic ammonium cations are dimethyl dioctadecyl ammonium, trimethyl octadecyl ammonium, dodecyl ammonium, hexadecyl ammonium, octadecyl ammonium, dioctadecyl morpholinium,  
40 1 - propyl - 2 - octadecyl imidazolinium and bis(- 2 - hydroxyethyl) octadecyl ammonium. These may be used singly or in combinations in order to produce an organo silicate of desired properties.

45 When substantially complete cation exchange is desired, it is preferred to employ from 0.9 to 1.4 equivalents of the organic cation, although on occasions it is found very advantageous to employ as much as 1.7 to  
50 1.8, and sometimes even up to 2.2 equivalents. However, when the clay has been synthesised at the higher pressures, viz. 700 to 1000 p.s.i., the above-quoted range may be,  
55 respectively, 0.6 to 1.4 and 1.0 to 2.2 equivalents.

The product can be separated by the usual steps of dewatering and drying, and then finally ground if desired. Normally the product will also be washed.

60 The processes described can employ as starting material the dried synthetic clay. However, when, as is preferred, the reaction is carried out in an aqueous medium, it is clearly advantageous to employ the

aqueous slurry, or cake-like mass, without drying. 65

Certain cation-modified clays in accordance with this invention possess oleophilic and gelling properties making them very useful materials in the preparation of, for example, lubricating greases. Others possess the ability to form organosols. 70

The following examples 10 to 14 are some examples of the preparation of organic derivatives of the new materials according to the invention. 75

#### EXAMPLE 10

11.25 gal. water was heated in the autoclave to boiling point and 21.8 lb. magnesium sulphate heptahydrate and 0.8 lb. lithium chloride were dissolved in it. A separate solution was made up consisting of 11.25 gal. water with 29.6 lb. sodium silicate of the type used in all other examples and 10.4 lb. anhydrous sodium carbonate. The second solution was gradually added to the first solution in the autoclave over a period of one hour. The mixture was then boiled at atmospheric pressure under continuous stirring for two hours, after which period the autoclave was sealed and heated to 207°C (250 p.s.i. pressure) in 4½ hours. The same temperature and pressure was maintained for 8 hours, then the heating was stopped and the mixture was allowed to cool below 100°C. It was then discharged from the autoclave. 80

1000 g. of the unwashed slurry from the autoclave containing 60 g. synthetic clay was diluted with 2 litre hot water. A solution of 50.8 g. (1.1 equivalents) of the material sold under the trade mark "Arquad 2HT—75%T" (which materials is dimethyl dioctadecyl ammonium chloride of 75% concentration in isopropanol) in 1.5 litre hot water was added to it under vigorous stirring. The mixture was heated to boiling point when it was observed that the dispersed solids were flocculated and settled on standing. The settled solids were filtered under vacuum, washed with hot water until the filtrate was substantially free of chloride and dried at 80°C for 2 hours. A soft pulverulent product was obtained which was easily ground to a fine powder suitable for use in manufacturing a grease. 85 90 95 100 105 110 115

#### EXAMPLE 11

The same procedure was followed as in Example 10 the only difference being that the autoclaving was continued for 24 hours. The resultant soft pulverulent product was even more suitable for use in manufacturing a grease. 120

#### EXAMPLE 12

The same procedure was followed as in Example 10 with the exception that the slurry from the autoclave was washed by filtration until the filtrate was substantially free from 125



sulphate. The filter cake was dried at 120°C for 8 hours and finely ground. 60 g. of the dried solids were dispersed in 3 litres hot water by mixing for 15 minutes and mixed with a solution 50.8 g. "Arquad" 2HT, continuing the preparation as described in Example 10.

Again a soft pulverulent product was obtained which was easily ground to a fine powder suitable for use in manufacturing a grease.

#### EXAMPLE 13

The same procedure was followed as in Example 10 with the exception that 74 g. (1.7 equivalents) of the "Arquad" 2HT was used. In this case the resultant product was suitable for the production of an organosol.

#### EXAMPLE 14

The product obtained in Example 6 was converted to organophilic form by dispersing 15 g. dry clay in 150 ml. hot water, adding a solution of 11.6 g. "Arquad" 2HT in 375 ml. hot water and continuing the preparation as described in Example 10.

The product was dispersed in a low viscosity lubricating oil and it was found that at 8—10% concentration stiff greases were obtained, similar in consistency to the lubricating greases in commercial use.

In general greases can be prepared by blending the organic ammonium clay-derivatives, in suitably finely divided form, with a wetting agent and a grease-base oil. The blending is preferably conducted as a milling operation and is advantageously in two steps, the first with a part of the required amount of grease-base oil, the second with the remainder. Finally the grease may be centrifuged to facilitate removal of trapped air-bubbles.

The greases comprise, in general, a major amount of grease-base oil and a minor amount, conveniently 2 to 29% by weight (suitably 5—15% and preferably 10%), of the organic clay-derivatives.

The following example 15 illustrates the manufacture of a grease:—

#### EXAMPLE 15

174 g. of light spindle oil (grade "Carnea" 21) was mixed with 4 g. methyl alcohol and 29 g. of the powder prepared previously in accordance with Example 10, was added to it. ("Carnea" is a trade mark). The mixture was stirred with a high shear mixer for 3 minutes, then passed through a colloid mill the shearing surfaces of which were set at 0.05 mm. clearance. After passing through the mill, 150 g. of the grease obtained, having a solids content of 14%, was mixed with 60 g. of the same kind of light spindle oil as used before, to reduce the solids content to 10%, and the mixture was once again passed through the colloid mill. After that,

the grease obtained was centrifuged to facilitate the removal of trapped air bubbles. The consistency of the grease was tested by a Gallenkamp miniature penetrometer using a cone of solid angle 90°, and having a total weight of 15.3 g. A value of 30 (one tenth millimetre units) was obtained.

In the preparation of organosols in accordance with the invention the organic ammonium compound employed for reaction with the synthetic swelling clay preferably has a chain of at least 18 C atoms and is used in an amount of at least 1.5 equivalents (preferably not more than 2.2) and suitably between 1.7 and 1.8. However, if the synthetic clay has been prepared at higher pressures, viz. 700 to 1000 p.s.i., then the amount of ammonium compound employed can be as little as 1.0 equivalents.

As a result, the product has substantially the whole of its exchangeable cations as organic cations. The remainder of the cations involved in the reaction (i.e. the 50% or more excess) are retained by the clay.

It seems that multilayer deposition of organic matter has taken place on the silica layer of the synthetic clay structure.

Such organic products are able to form organosols with liquid aliphatic and aromatic hydrocarbons, especially petroleum ether, white spirit, benzene, toluene and xylene. They are organosols with a disperse phase of substantial inorganic content. When the organosol is mixed with water or an aqueous solution and shaken, it forms an aqueous emulsion in which, generally, the organic liquid is the outer phase.

#### EXAMPLE 16

An organic clay-derivative was prepared in accordance with Example 10 above but employing 74 g (1.7 equivalents) of the amine.

The product was wetted with methyl alcohol and dispersed in toluene at 8% concentration. A clear sol of low viscosity was formed. The sol was stable between 0°C and 100°C. When part of this sol was mixed with half of its volume of water and shaken for one minute, a stiff emulsion was obtained in which the outer phase was toluene.

Natural hectorite does not form sols or water/organic solvent emulsions.

The inorganic swelling clays of the invention, i.e. those where M is Na or Li, can be used on their own but ease of introduction into various media can be facilitated by use of a peptising agent.

Thus in accordance with a further feature of the invention, the inorganic clays having the general formula quoted when M is Na or Li, may be formed into a composition with up to 25% (by weight of the material) of one or more peptizers selected from alkali metals salts having polyvalent anions. Prefer-

ably the cation M of the material is Na<sup>+</sup> or Li<sup>+</sup>. Alternatively organic materials can be employed as peptising agents, for example, quebracho or a lignosulphonate.

- 5 Preferably the quantity of peptizer present is from 3% to 12% (by weight of the clay), suitably from 5 to 10%, and advantageously 5% or 6%. These quantities are especially suitable when the peptizer is tetrasodium pyrophosphate.

10 Among other peptizers which may be employed are the product sold under the Trade Mark "Calgon" and sodium tri-poly-phosphate. In general the most suitable peptizers are sodium salts having polyvalent anions, which anions are capable of forming either complex or insoluble salts with magnesium.

15 These compositions can be conveniently prepared by dry-blending the synthetic clay-like mineral and the peptizer. Particle size of the resultant blend is not critical, being chiefly dependent upon the use to which the blend is to be put.

20 It may be found desirable on occasions for the compositions to contain also small amounts of one or more additives, the nature of which will be dictated by the use to which the final composition is to be put.

25 Certain of the compositions, for example those in which the cation M is Na<sup>+</sup> or Li<sup>+</sup>, have the unexpected property of possessing the ability to form substantially transparent colloidal dispersions in the form of sols when mixed with water. Aqueous sols, whether made from these compositions themselves, or directly from the constituents of them, represent a further feature of the present invention, and can have a total solids content (synthetic material+peptizer) of up to 30 10% although normally 2 to 66% is a convenient solids content. Such sols cannot be

obtained from naturally occurring swelling clays. In practice the sols provide an easy method of introducing the synthetic swelling clay into the medium in which that clay is required.

45 Although dilute aqueous dispersions of the kind just described do not show any thixotropy or appreciable Bingham Yield Value, both these properties may be developed by mixing with specific reagents. Such a property renders composition and/or sols in accordance with this invention especially suitable for use in emulsion paint media, for example polyvinyl acetate paint medium.

50 Indeed it is found that in this connection the compositions are very effective gelling agents, as also are the lithium-containing clays when employed without the peptising agent.

55 A further application of the synthetic clays, and blends thereof with a peptising agent, lies in the bonding of foundry sands.

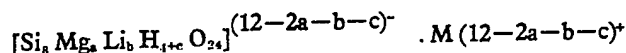
60 Samples of the sodium form clays, alone and with 6% tetrasodium pyrophosphate were taken. 5 parts of each were mixed with 100 parts of silica sand and 3.5 parts of water, and then milled for 5 mins.

65 A commercially available grade of a natural swelling clay was treated in the same way.

70 It was found that the two synthetic-clay containing sand-mixes had green strengths 50% better than that of the natural clay sand-mix. The refractoriness (as measured by their fusion temperatures in an electric refractory furnace) of all samples was substantially equal, at approximately 1300°C.

#### WHAT WE CLAIM IS: —

1. A synthetic silicate having a structure similar to that of clay minerals of the smectite type and having the general formula



having

- 85 (i) M as a sodium, a lithium or an equivalent of an organic cation, and  
(ii) the value of a, b and c such that either

$$a < 6; b > 0; c > 0;$$

and

90  $b + c < 2; \pm(a + b + c - 6) < 2;$

or

$$a < 6; b = 0; \pm c < 2;$$

and

$$\pm(a + c - 6) < 2$$

- 95 (iii) a cation exchange capacity of 50 to 120 m.e.q./100g,  
(iv) when M is Na<sup>+</sup> or Li<sup>+</sup>, a Bingham Yield Value of from 40 to 250 dynes/cm<sup>2</sup> as a 2% w/v dispersion in tap water.

2. A synthetic silicate as claimed in claim 1 wherein M is Na<sup>+</sup> and

- (i) a is 5.29; b is 0.47 and c is 0.49; or  
(ii) a is 5.03; b is 0.63 and c is 0.78; or  
(iii) a is 5.09; b is zero and c is 1.38.

3. A synthetic silicate according to claim 1 or claim 2 which, when M is Na<sup>+</sup> or Li<sup>+</sup>, has a Bingham Yield Value of from 50 to 250 dynes/cm<sup>2</sup> as a 2% w/v dispersion in tap water.

4. A synthetic silicate according to any preceding claim wherein b is from 0.6 to 1.05.

5. A synthetic silicate according to any preceding claim wherein b is zero and a is from 5.0 to 5.8.

6. A synthetic silicate according to claim

1 substantially as herein described and with reference to Examples 1, 2 or 5.

7. A synthetic silicate according to claim 1 substantially as herein described and with reference to Examples 6 or 7.

8. A composition comprising a synthetic silicate according to any of claims 1 to 7 in which M is a sodium or lithium cation, in admixture with up to a total of 25% by weight of the synthetic silicate of one or more peptizers selected from alkali metal salts having polyvalent anions.

9. A composition according to claim 8 comprising up to a total of 5% of the peptizer.

10. A composition according to claim 9 in the form of an aqueous sol having up to 10% solids content.

11. A composition according to any of claims 8 to 11 in which the synthetic silicate is a synthetic silicate according to claim 3.

12. A composition according to claim 8 substantially as herein described.

13. A synthetic silicate according to any of claims 1 to 5 wherein M is an organic ammonium cation having at least 10 carbon atoms.

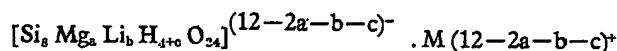
14. A synthetic silicate according to claim 13 wherein the cation has at least 18 carbon atoms.

15. A synthetic silicate according to claim 14 in which the cation is dimethyl dioctadecyl ammonium.

16. A synthetic silicate according to claim 3 wherein M is an organic ammonium cation as defined in any of claims 13 to 15.

17. A synthetic silicate according to claim 13 substantially as herein described with reference to any of Examples 10 to 16.

18. A process for the synthesis of a synthetic silicate having a structure similar to that of clay minerals of the smectite type and having the general formula



having

(i) M as a sodium, a lithium or an equivalent of an organic cation, and

(ii) the value of a, b and c such that either

$$a < 6; b > 0; c > 0;$$

and

$$b + c < 2; \pm(a + b + c - 6) < 2;$$

or

$$a < 6; b = 0; \pm c < 2;$$

and

$$\pm(a + c - 6) < 2$$

the process comprising

(i) precipitating a magnesium silicate having the value of "a" desired in the said synthetic silicate by combining an aqueous solution of a water soluble magnesium salt with an aqueous alkaline solution of one or more sodium compounds in the presence of dissolved silicon-delivering material, the pH of the alkaline solution being maintained at 8 to 12.5 throughout,

(ii) without first drying or washing this precipitate heating it at a temperature of at least 170°C and a pressure of at least 100 p.s.i., the temperature being less than 370°C and such that a liquid phase is present, until crystal growth occurs, and

(iii) separating the resultant solid and liquid phases.

19. A process according to claim 18 in which the magnesium silicate precipitate obtained in Step (1) is a magnesium lithium silicate having the values for a and b desired in the desired synthetic silicate being produced by the process, and in which the combina-

tion of the alkaline solution with the magnesium salt solution is conducted in the presence also of an aqueous solution of a lithium salt.

20. A process according to claim 18 or claim 19 wherein the coprecipitation is effected by mixing a hot solution containing (i) the magnesium salt and (ii) the lithium salt if employed, with a cold solution containing (i) the silicon-delivering material (ii) the sodium compound required for maintaining the alkaline pH.

21. A process according to any of claims 18 to 20 wherein the concentrations of the reactants are selected such that the concentration of the resultant precipitate is not substantially in excess of 5% by weight.

22. A process according to any of claims 18 to 21 wherein the precipitate formed in step (i) is boiled before being heated under pressure in step (ii).

23. A process according to any of claims 18 to 22 comprising the additional steps of washing the solid phase to remove soluble by-products and drying the washed silicate.

24. A process according to claim 23 comprising the additional step of reacting the washed solid phase, in which the cation M is sodium, before or after drying, with a lithium compound whereby the exchangeable sodium cation M is replaced by lithium.

25. A process according to claim 23 comprising the additional step of reacting the washed solid phase in which the cation M is sodium, before or after the drying, with an organic ammonium salt whereby the exchangeable sodium cation M is replaced by an equivalent of organic ammonium cation.

26. A process according to claim 25 in

which the organic ammonium cation is one having at least 10 carbon atoms.

27. A process according to claim 26 in which the organic ammonium cation is one having at least 18 carbon atoms.

28. A process according to claim 27 in which the organic ammonium cation is dimethyl dioctadecyl ammonium.

29. A process according to claim 18 substantially as herein described and with refer-

ence to any of Examples 1, 2, 5, 6, 7 or 10 to 16.

30. A synthetic silicate prepared by a process according to any of claims 18 to 29.

For the Applicants:  
GILL, JENNINGS & EVERY,  
Chartered Patent Agents,  
51/52 Chancery Lane,  
London, W.C.2.

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1970.  
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from  
which copies may be obtained.

**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

**BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☐ **FADED TEXT OR DRAWING**
- ☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☒ **GRAY SCALE DOCUMENTS**
- ☐ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**